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Dissociative electron attachment to the highly reactive difluoromethylene molecule—importance of CF_2 for negative ion formation in fluorocarbon plasmas

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Dissociative electron attachment to the highly reactive difluoromethylene molecule—importance of CF_2 for negative ion formation in fluorocarbon plasmas

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Abstract. Dissociative electron attachment to the highly reactive difluoromethylene molecule, CF_2 , produced in a $\text{C}_3\text{F}_6/\text{He}$ microwave plasma and step-wise via the fast atom reaction $\text{CF}_3\text{I} + \text{H} \rightarrow \text{CF}_3 + \text{HI}$ and $\text{CF}_3 + \text{H} \rightarrow \text{CF}_2 + \text{HF}$, has been investigated. The upper limit for the cross section of formation of F^- via dissociative electron attachment to CF_2 is estimated to be $5 \times 10^{-4} \text{ \AA}^2$. This value is four orders of magnitude smaller than the cross section previously predicted from scattering calculations. It is concluded that difluoromethylene plays a negligible role in negative ion formation in fluorocarbon plasmas.

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1. Introduction

Fluorocarbon gases are widely used in plasma etching. The etching characteristics depend on highly reactive radicals and molecules, such as CF and CF_2 , and positive and negative ions present in the discharge. Difluoromethylene, CF_2 , is the most abundant molecular radical species present in many industrially relevant fluorocarbon plasmas [1, 2], where it is known to play an important role in film deposition and etching [3] and polymerization reactions leading to the formation of undesired macromolecules [2].

The negative ion density in such a discharge can be orders of magnitude larger than the electron density [4]. Therefore, negative ions play a significant role in changing the distribution and concentration of charged species in a plasma and thereby considerably influence the ion chemistry taking place.

The importance of the highly reactive CF_2 molecule for the formation of negative ions in fluorocarbon discharges is still unknown, perhaps due to the difficulty of producing and investigating this short-lived, unstable molecule. CF_2 is stable as an isolated molecule, but is highly reactive and must be generated *in situ* for experimental investigations. If the highly reactive CF_2 molecule possesses an attachment resonance or resonances at electron energies below 10 eV, attachment of plasma electrons with typical energies of several electronvolts could lead to the formation of F^- and possibly also CF^- , C^- and F_2^- anions. For the formation of the stable parent anion, CF_2^- , an efficient collision mechanism for de-excitation of the transient anion CF_2^{*-} has to be available; the lifetime of the transient anion is otherwise expected to be in the picosecond range or lower.

Electron scattering calculations performed by Rozum *et al* predicted the formation of F^- to proceed through a 2B_1 resonance state with a maximum at 0.95 eV and a width of 0.18 eV. The attachment cross section for CF_2^{*-} formation was estimated to be 25.76 \AA^2 ; it was predicted that about 5% of the formed transient parent CF_2^{*-} anions subsequently dissociate to form $F^- + CF$ [5]. Lee *et al* [6] found evidence for a 2B_1 shape resonance at a slightly higher electron energy of 1.5 eV. A study by Francis-Staite *et al* [7], however, places this resonance considerably lower at less than 0.1 eV. Francis-Staite *et al* found that polarization has a critical effect in

the calculated resonance position; they suggest that the higher energies predicted by Rozum *et al* and Lee *et al* could be explained if less polarization had been taken into account in their calculations.

A recent paper presenting calculations assessing the importance of electron attachment to CF_2 in CF_4 plasmas called for an experimental investigation of electron attachment to CF_2 [8]. There are few previous experimental investigations of low-energy electron collisions with CF_2 because of its high reactivity. Maddern *et al* [9] and Francis-Staite *et al* [7] have observed low-energy elastic electron scattering by CF_2 .

2. Experiment

The experimental setup, the electron radical interaction chamber (ERIC), has been described previously [10]. Briefly, low-energy electrons from a trochoidal electron monochromator collide with sample molecules in a differentially pumped interaction region. The electron beam is pulsed; when all electrons have left the interaction region, any ions formed are extracted into a time-of-flight (TOF) mass spectrometer. Both positive and negative ions can be observed by reversing the electric fields in the TOF spectrometer. The electron energy scale for the positive spectra was determined using the ionization thresholds of He (24.6 eV) and HF (16.0 eV) [11]. The energy scale for the negative ions formed by dissociative electron attachment to the parent gas was determined using the SF_6^{*-} peak at 0 eV from electron attachment to SF_6 and with the S^- peak from CS at 5.43 eV (see [12]), and the CN^- peak from CF_3CN at ~ 1.3 eV [13]. The uncertainty in the electron energy scale is estimated to be ± 0.2 eV. The electron energy resolution is ~ 200 meV, measured from the full width half maximum (FWHM) of the SF_6^{*-} peak at 0 eV.

CF_2 was produced by passing a mixture of C_3F_6 and He through a microwave discharge and by reaction of hydrogen atoms with CF_3I . The plasma region where reactive species are produced is separated by about 25 cm of glass tube from the interaction region. Therefore, the number of vibrationally and electronically excited and very short-lived radical states will be greatly reduced in the interaction region compared to the plasma volume. Frequently in measurements with the $\text{C}_3\text{F}_6 + \text{He}$ plasma, it appeared that the electron current below 300 meV close to 0 eV was reduced, perhaps due to reactive species affecting surfaces in the monochromator. Therefore, peaks close to 0 eV electron energy may be cut off or show distorted shapes. The energy scale for the negative ions formed by dissociative electron attachment with the $\text{C}_3\text{F}_6 + \text{He}$ plasma running was calibrated with CS and CF_3CN because of this distortion at 0 eV.

CF_2 was also produced in the stepwise fast atom reaction,



and



Atomic hydrogen was produced in a H_2/He microwave discharge again located 25 cm from the interaction region. The $\text{H}/\text{H}_2/\text{He}$ mixture was mixed with CF_3I 4–8 cm from the interaction region.

Alternative methods can be used for the generation of CF_2 . For example, a clean sample of CF_2 can also be produced via pyrolysis of C_2F_4 [7, 9].

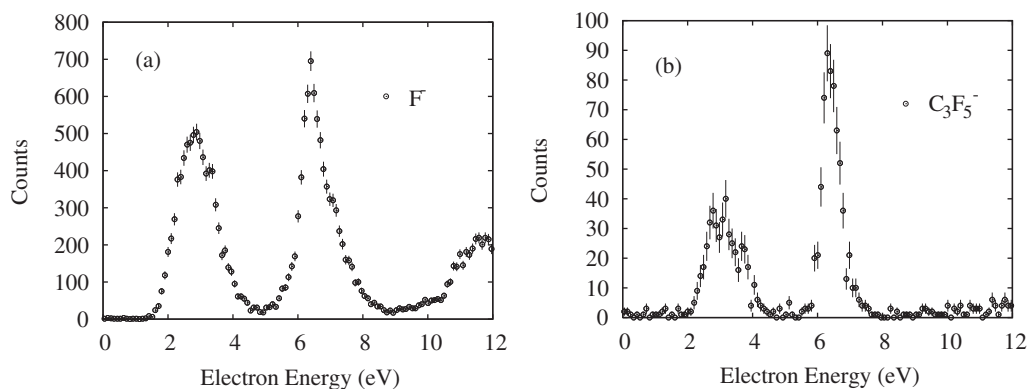


Figure 1. Integrated signals of (a) F^- and (b) $C_3F_5^-$ formed in dissociative electron attachment to C_3F_6 .

3. Results and discussion

3.1. Dissociative electron attachment to the parent gas molecule, C_3F_6

Dissociative electron attachment to C_3F_6 has been investigated for comparison with attachment to the gas sample produced in the microwave discharge of $C_3F_6 + He$. Anions detected were F^- , CF_3^- , $C_2F_3^-$ and $C_3F_5^-$, with F^- and $C_3F_5^-$ being the most abundant. Integrated signals of the strongest F^- and $C_3F_5^-$ anions are shown in figures 1(a) and (b). F^- is formed at three positions with maxima at 2.9 ± 0.2 , 6.4 ± 0.2 and $\sim 11.6 \pm 0.3$ eV. $C_3F_5^-$ has its peak maxima at $\sim 3.2 \pm 0.2$ and 6.3 ± 0.2 eV and $C_2F_3^-$ around 3.5 and 6.0 eV. Furthermore, CF_3^- is formed at an electron energy of ~ 6.5 eV. The positions of the peak maxima and the relative peak ratios of the different anions observed here are in good agreement with literature values [14, 15] within experimental uncertainties.

3.2. C_3F_6/He plasma composition

In figure 2(a), a positive mass spectrum of the C_3F_6/He parent gas at 15 eV electron energy with the plasma off is shown. $C_3F_6^+$, the parent molecular ion, is the most intense signal and the fragments $C_2F_4^+$ and $C_2F_5^+$ are also visible. In figures 2(b) and (c), positive mass spectra recorded at 15 eV with the plasma on and at two different pressure conditions are shown. Here, (b) was taken at a lower pressure than (c). In the case of low pressure (b), the plasma etches the Pyrex glass tube at the position of the microwave cavity and Si^+ dominates the positive mass spectrum together with the CF_2^+ and CF_3^+ ions. The Cl^+ signal visible in figure 2(b) originates from Cl atoms that are formed in the discharge from a residue of CCl_4 in the chamber. The $C_3F_6^+$ signal was found to be weak under all pressure conditions, which implies that the C_3F_6 parent gas is efficiently converted into other species in the discharge. At higher pressure in (c), the Si^+ signal is weaker than at low pressure (b) and CF_2^+ dominates the positive spectrum. Weak signals of larger ions with masses up to ~ 300 amu are also visible in positive spectra (b) and (c).

To alter the plasma composition further, C_3F_6/He was mixed with SF_6 . In figure 2(d), a positive mass spectrum obtained from a plasma produced with this gas mixture is shown. CS^+ and CS_2^+ are present together with several other sulphur, fluorine and/or carbon-containing ions. CS was subsequently used as a reference molecule in section 3.3 to calculate the CF_2

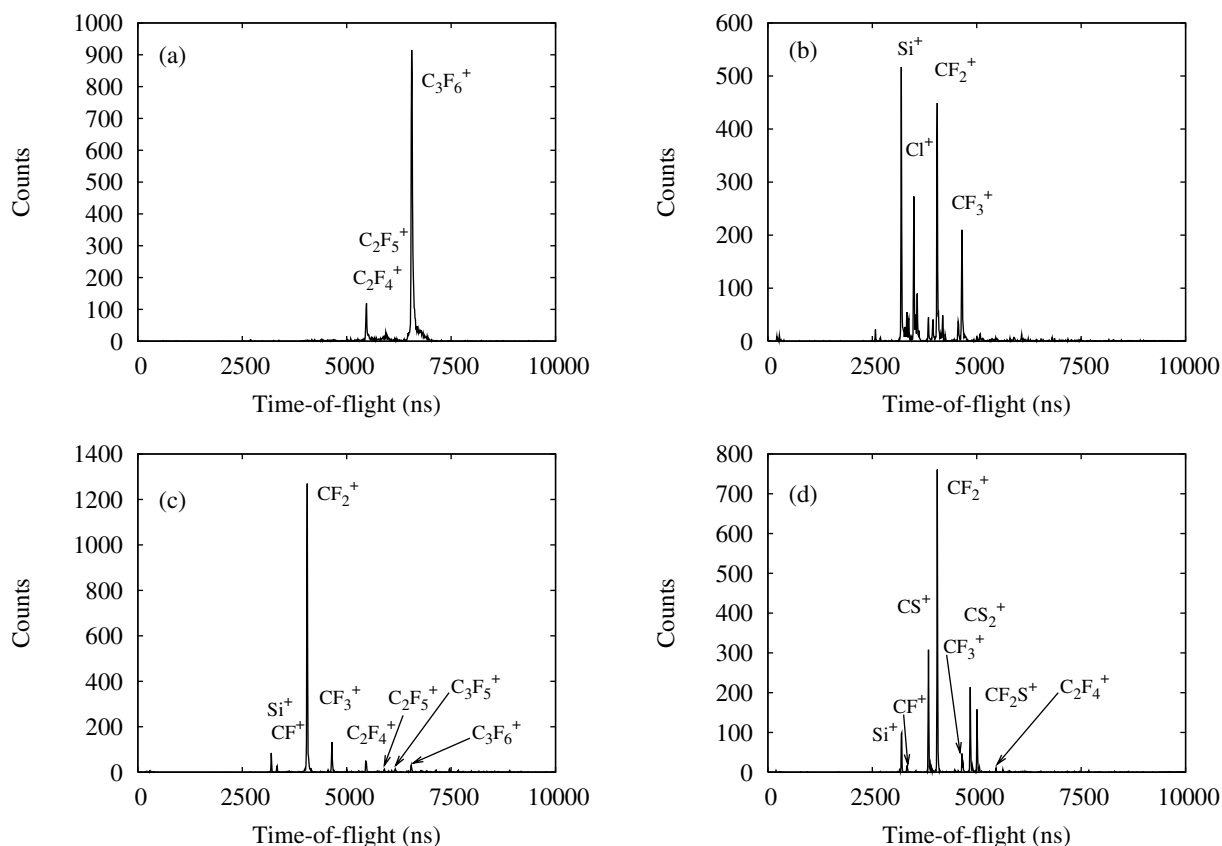


Figure 2. Positive ions formed by electron impact ionization in the $\text{C}_3\text{F}_6/\text{He}$ gas mixture (a) with the plasma off, (b) with the plasma on at low and (c) high C_3F_6 inlet pressure and (d) with a SF_6 admixture. The electron energy is ~ 15 eV in all spectra.

attachment cross section as its attachment peaks and absolute cross sections had been measured previously [12].

HF^+ from HF is found in all positive spectra and its formation was enhanced by the addition of SF_6 . HF is probably formed in plasma reactions of plasma species with residual water molecules. The ionization threshold of HF was used to calibrate the positive electron energy scale. HF^+ is not visible in the mass spectra presented in figures 2(b)–(d) taken at 15 eV as the ionization threshold of HF is at 16 eV [11].

In order to confirm that the CF_2^+ signal observed in the positive mass spectra is caused by ionization of the CF_2 molecule, the appearance potential of the CF_2^+ signal was measured. The integrated CF_2^+ signal as a function of electron energy is shown in figure 3. The CF^+ and CF_3^+ ion curves are shown in the same figure for comparison. CF_2^+ can unambiguously be identified to originate from electron impact ionization of the CF_2 molecule as its curve shows a clear onset at the known ionization energy of the CF_2 molecule, 11.44 eV [11]. This implies that CF_2 is indeed present in the gas stream. By contrast, CF^+ and CF_3^+ originate mainly from the fragmentation of larger molecules as the positive ion yield is small below ~ 16 eV while their ionization thresholds are low at 8.9–9.4 eV (CF) and 8.6–9.8 eV (CF_3) [11].

The positive ion onset curve can also reveal the presence of excited molecules as the ionization thresholds of electronically or vibrationally excited states are, of course, lower than

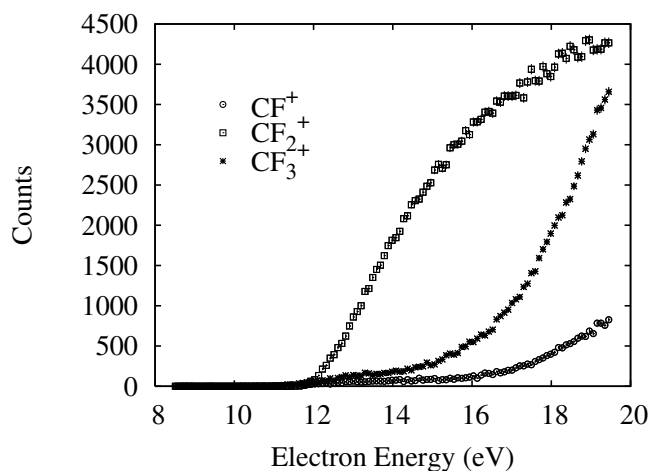


Figure 3. Typical ionization curves of CF^+ , CF_2^+ and CF_3^+ obtained experimentally. The CF_2 molecule can be identified clearly from the onset of the curve at its ionization threshold, 11.44 eV [11]. By contrast, the detected CF^+ and CF_3^+ ions mainly originate from the fragmentation of larger molecules and not from ionization of CF and CF_3 .

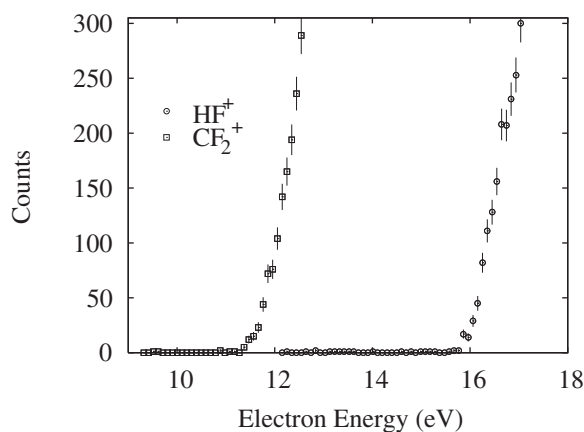


Figure 4. HF^+ and CF_2^+ ionization onsets in detail. There is no significant contribution from vibrationally or electronically excited states in either onset. Excited states may therefore only be present as traces (see text).

ground state thresholds [16]. The ionization onsets of CF_2 and HF recorded experimentally are shown in more detail in figure 4. It can be concluded that at most a trace of electronically excited CF_2 molecules may have been present, as no CF_2^+ signal is observed below the ionization threshold of the ground state CF_2 molecule. The electron energy resolution of the present experiment is not sufficient to detect moderate vibrational excitation, but it is clear that there is no significant contribution of CF_2 molecules to the sample with >200 meV of vibrational excitation energy; the energies of the CF_2 vibrational normal modes are ν_1 (symmetric stretch) 152 meV, ν_2 (bend) 82 meV and ν_3 (antisymmetric stretch) 138 meV [17]. Vibrational excitation can lead to considerable shifts in dissociative electron attachment peak maxima positions and enhancements of cross sections [18].

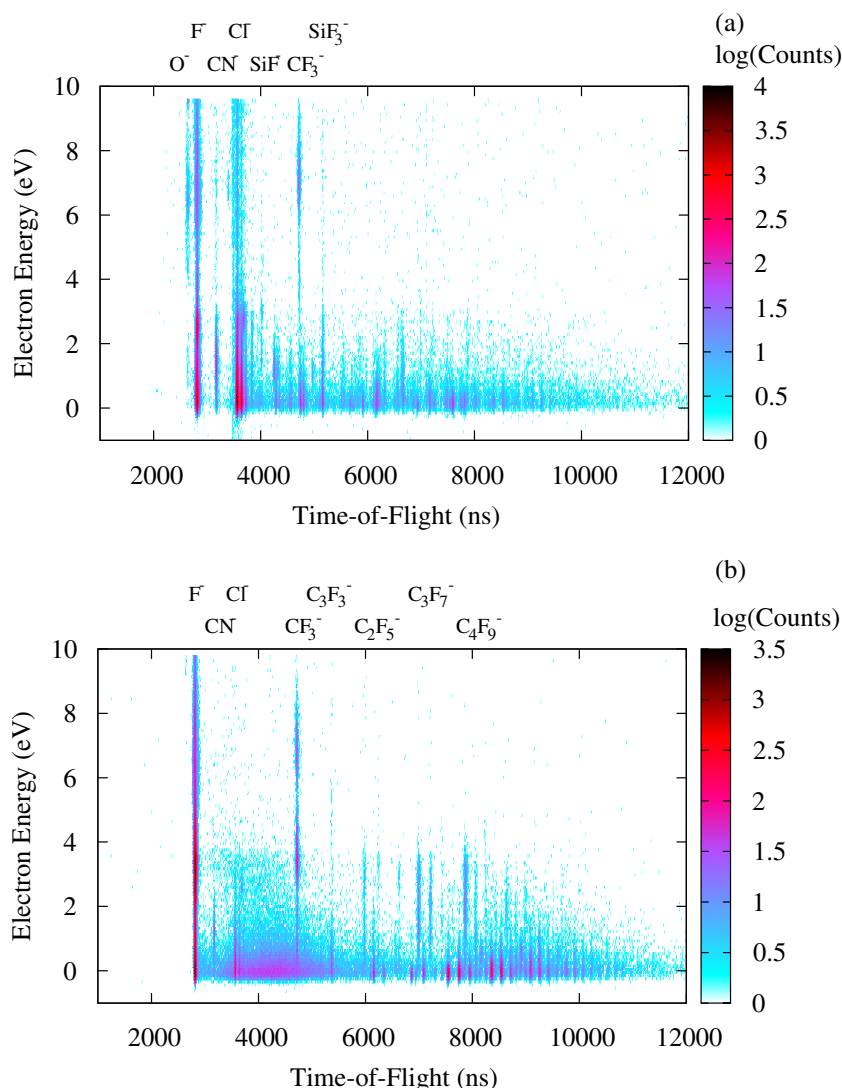


Figure 5. Negative ions observed in dissociative electron attachment to species formed in a $\text{C}_3\text{F}_6/\text{He}$ plasma at two different pressure conditions. In (a) the C_3F_6 inlet pressure is low while in (b) the pressure is higher.

3.3. Negative ion mass spectra—assignment of attachment peaks to CF_2

Dissociative electron attachment to $\text{C}_3\text{F}_6/\text{He}$ plasma species was investigated under a number of different pressure and discharge conditions. Two exemplar data sets are shown as two-dimensional plots (2D) in figures 5(a) and (b). In figure 6 a 2D plot of the negative ions formed in the $\text{C}_3\text{F}_6/\text{He}/\text{SF}_6$ gas mixture is shown. The S^- and C^- bands from dissociative electron attachment to CS are clearly visible between 5 and 7 eV [12].

Apart from the $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ anions, which were observed in some measurements due to residual CCl_4 in the chamber, F^- was the most intense anion in all data sets recorded shown in figures 5 and 6. Furthermore, CF_3^- formation takes place at electron energies of ~ 3 eV and ~ 7 eV, and many heavier anions appear mainly close to 0 eV.

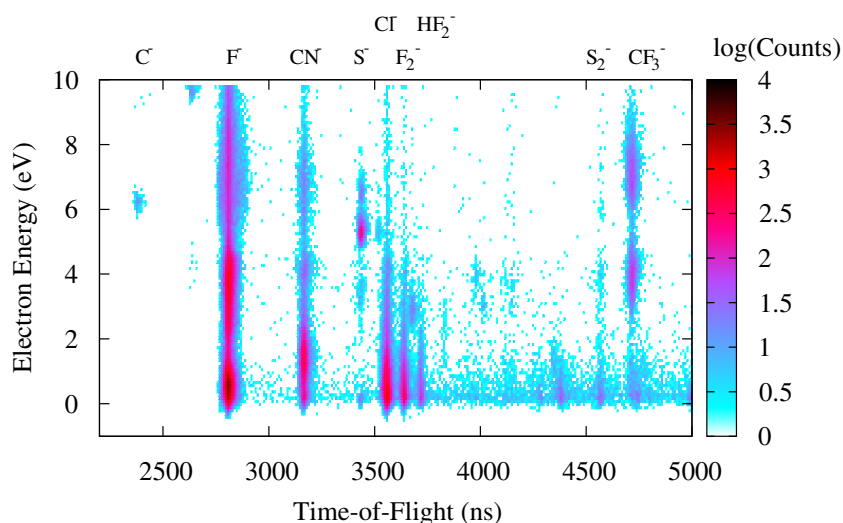


Figure 6. 2D plot of the negative ion spectra recorded in the C_3F_6/SF_6 plasma. It resembles figure 5 but now additional anions, C^- (at ~ 6 eV) and S^- (between ~ 5 and 7 eV), from dissociative electron attachment to CS are visible in the spectrum.

It is clear from the data presented so far that many different species are produced in the discharge that give negative ions upon electron attachment. The present discussion of the data will concentrate on CF_2 . As mentioned above, dissociative electron attachment to CF_2 may lead to the formation of C^- , F^- , F_2^- and CF^- . The thermodynamic thresholds for the formation of CF^- and F^- from ground state CF_2 can be calculated using the dissociation energy of the CF–F bond, ≥ 5.20 eV [19], and the electron affinities of CF ($> 3.30 \pm 0.30$ eV [11]) and F (3.40 eV [11]) as $AE(CF^-) \sim 1.90$ eV and $AE(F^-) \geq 1.80$ eV. Calculation of the CF–F bond energy using the heats of formation of CF_2 (-182 kJ mol $^{-1}$ [11]), F (79.39 kJ mol $^{-1}$ [11]) and CF (255.22 kJ mol $^{-1}$ [11]) yields a value of 5.36 eV, which leads to similar results, $AE(CF^-) > 2.06$ eV and $AE(F^-) = 1.96$ eV. The experimental literature result for the electron affinity of CF is significantly larger than the values predicted by theoretical calculations of between ~ 0.5 and 1.2 eV [20]. Using the theoretical CF electron affinity increases the threshold for the formation of CF^- by at least 2 eV.

The thresholds for the formation of $C^- + F_2$, ≥ 7.73 eV, and $F_2^- + C$, ~ 5.87 eV, are considerably higher than those for F^- and CF^- . These thresholds have been calculated from the electron affinities of C (1.26 eV [11]) and F_2 (~ 3.12 eV [11]), the bond energy of F_2 (1.41 eV [21]) and the assumption that breaking the two C–F bonds of CF_2 requires twice the CF–F bond energy.

Integrated anion signals of F^- and CF_3^- at four different pressure and discharge conditions are shown in figures 7(a) and (b). F^- is observed with maxima at ~ 0 eV, 2.45 eV, ~ 3.5 eV and ~ 7 eV. Any of the F^- peaks above ~ 2 eV could in principle originate from dissociative electron attachment to CF_2 . CF_3^- is observed with maxima at 0 eV, ~ 3.6 eV and ~ 7 eV. Note that most of the CF_3^- signal close to 0 eV originates from the overlapping band of noise probably produced by metastable dissociation events and also partly from overlapping Cl_2^- .

It is interesting to note that no traces of C^- or CF^- are observed in the negative mass spectra (see figure 5(b)). This means that these negative ions are not formed in dissociative

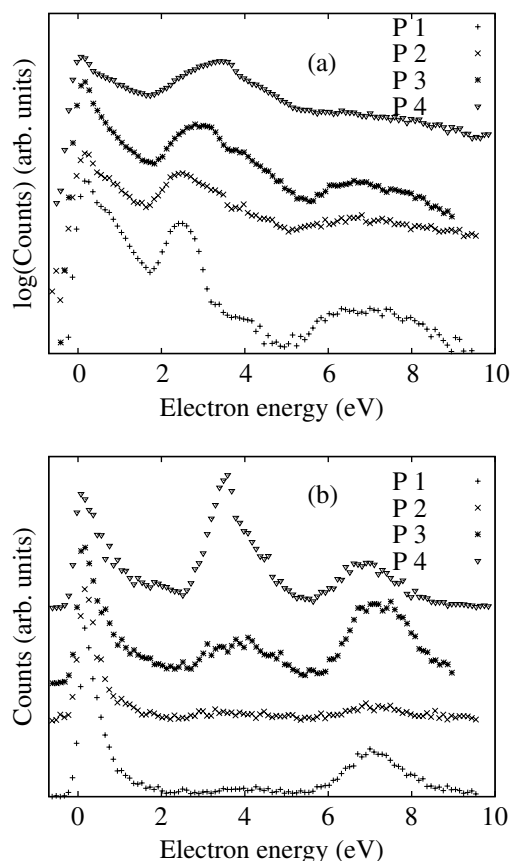


Figure 7. F^- (a) and CF_3^- (b) at four different pressure and discharge conditions. The pressures relate to each other as $P1 < P2 < P3 < P4$. The F^- signal at 0 eV and between 2 and 4 eV consists of overlapping peaks. Note that most of the CF_3^- signal close to 0 eV in (b) originates from an overlapping band of noise from metastable dissociation processes and also partly from an overlapping Cl_2^- signal. (a) is a logarithmic plot to increase the visibility of the weaker F^- peaks; (b) is a linear plot.

electron attachment to CF_2 or the cross section for their formation is so small that they cannot be detected in this experiment. F_2^- is observed with a maximum at ~ 2.8 eV (see figure 6). This is more than 2 eV below the calculated appearance energy of F_2^- from CF_2 and practically excludes CF_2 as a possible candidate for the formation of the detected F_2^- . This leaves only the F^- peaks, which could be formed by dissociative electron attachment to CF_2 .

F^- appears with a maximum close to 0 eV and there is also sometimes a shoulder in the peak at ~ 0.7 eV (see figure 7(a)). The interpretation of this signal is difficult. The F^- signal below 1 eV consists of two or more overlapping peaks from different parent molecules, the concentration of which may change from measurement to measurement, thus influencing the F^- peak, as visible in figure 7(a). F_2 is one possible candidate for the formation of F^- at electron energies near 0 eV, despite being observed only very weakly in the positive mass spectra. F_2 has a very small ionization cross section for the formation of F_2^+ at 20 eV electron energy of 0.047 \AA^2 [22]. By comparison, the ionization cross section of CF_2 is one order of magnitude

larger, 0.529 \AA^2 [23], at 20 eV. F^- formation from F_2 could be detectable in the negative spectra because the cross section for the formation of F^- in dissociative electron attachment to F_2 close to 0 eV is very large, 80 \AA^2 [24].

Saturated fluorocarbons with up to six carbon atoms are known to have a thermodynamic threshold of at least 1.2 eV for F^- formation but form long-lived parent anions at 0 eV [25]. There is little data about dissociative electron attachment to unsaturated species available, but it may be possible that dissociative electron attachment to these larger molecules leads to the formation of F^- if the C–F bond strength is lower than in the saturated compounds.

The intensities of negative ion peaks in the dissociative electron attachment spectra have been compared between the data sets of the different measurements made. If the relative intensities of two dissociative electron attachment peaks are constant under several different pressure and discharge conditions, then it is likely that these peaks are correlated and the negative ions are formed in dissociative electron attachment to the same parent molecule. Similarly, signals from positive and negative ion spectra recorded under identical conditions are compared to identify the parent molecules responsible for dissociative electron attachment processes.

A change in the intensity of a positive parent ion of each molecule should be accompanied by a similar change in the intensity of the dissociative electron attachment peaks that originate from the same molecule.

The change in the ratio of the intensities of two parent positive ions, I_{A^+} to I_{B^+} , between two different conditions p_1 and p_2 should be equal to the change in ratios of the intensities of the negative ions formed by the same molecules, I_{a^-} to I_{b^-} , between p_1 and p_2 in the negative ion spectrum. This relationship can be represented by [10, 12]

$$\frac{I_{\text{A}^+}(p_1)/I_{\text{B}^+}(p_1)}{I_{\text{A}^+}(p_2)/I_{\text{B}^+}(p_2)} = \frac{I_{\text{a}^-}(p_1)/I_{\text{b}^-}(p_1)}{I_{\text{a}^-}(p_2)/I_{\text{b}^-}(p_2)}. \quad (3)$$

Calculations are made of $I_{\text{A}^+}/I_{\text{B}^+}$ from the experimental data to compare the intensity of each parent ion A^+ in the positive ion mass spectra with the parent B^+ ion of a ‘reference’ molecule B. A reference molecule is a molecule present in the gas sample with known electron attachment bands. For each new dissociative electron attachment peak considered, calculations are made of the ratio $I_{\text{a}^-}/I_{\text{b}^-}$, where I_{a^-} is the unidentified electron attachment peak intensity and I_{b^-} denotes the peak intensity of the electron attachment peak of the reference molecule.

Comparison of dissociative electron attachment peaks showed that the F^- peak visible at 2.45 eV at low pressures is correlated with the F_2^- peak at 2.8 eV and an SiF_3^- peak close to 0 eV. Integrated signals of these three anions are shown in figure 8. These peaks probably originate from dissociative electron attachment to Si_2F_6 , which may be formed in plasma etching of the Pyrex glass tube. Using the heats of formation of Si_2F_6 ($-2383.29 \text{ kJ mol}^{-1}$) [26] and SiF_3 ($-1085.33 \text{ kJ mol}^{-1}$) [11], the Si–Si bond energy is calculated to be 2.2 eV. As the electron affinity of SiF_3 is $\sim 2.4 \text{ eV}$ [11], the dissociation channel involving the formation of SiF_3^- is exothermic. A recent calculation yields an $\text{Si}_2\text{F}_5\text{–F}$ bond dissociation energy of 6.53 eV [27]. As the electron affinity of F is 3.40 eV [11], this leads to a thermodynamic threshold of F^- formation of 3.13 eV, which is $\sim 0.6 \text{ eV}$ above the observed peak maximum.

Further evaluation of peak intensities showed that at higher pressures the F^- peak at 3.5 eV and the CF_3^- peak at 3.6 eV are roughly correlated in intensity. Those peaks are fairly broad and may originate from dissociative electron attachment to several species, most likely longer fluorocarbon molecules formed by polymerization reactions in the discharge. The F^- and CF_3^-

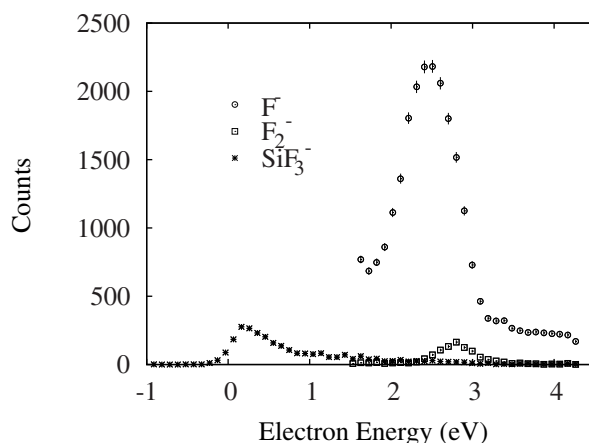


Figure 8. Integrated signals of the F^- , F_2^- and SiF_3^- anions observed in the dissociative electron attachment spectra at low gas pressure. The peaks shown in the figure originate from the same parent molecule, probably Si_2F_6 , as their relative intensity ratios are constant when the pressure is changed. The F^- peak is only clearly distinguishable at very low gas pressures. The F^- and the F_2^- signals below ~ 1.5 eV are not shown as they originate from dissociative electron attachment to other molecules (see text).

bands observed here correspond to bands observed at a similar energetic position in a C_4F_8 ECR plasma [28]. Stoffels *et al* [29] observed F^- at ~ 3 eV in a CF_4 plasma. They concluded that this peak is likely to originate from dissociative electron attachment to C_2F_6 and C_3F_8 [29]. A number of further molecules are known to have attachment bands leading to the formation of F^- and CF_3^- between 3 and 4 eV, among them C_2F_4 [30], C_2F_6 [25], C_3F_8 [25], C_4F_8 [28] and $n-C_4F_{10}$ [25].

The F^- peak at 6.8 eV and the CF_3^- peak at 7.5 eV were also found to be correlated in intensity. These peaks most likely originate from CF_4 [25, 29, 31]. An F^- peak was also observed in an experiment, where gas was sampled from a CF_4 plasma, at a comparable energetic position [29].

This analysis suggests that none of the dissociative electron attachment processes observed is due to CF_2 .

3.4. Calculation of the maximum dissociative electron attachment cross section of CF_2

A method to calculate dissociative electron attachment cross sections in gas mixtures has been described previously [12]. Briefly, the absolute dissociative electron attachment cross section, σ_A^- , of a new molecule, A, is estimated by comparison with a reference molecule, B, with known dissociative electron attachment and electron impact ionization cross sections, which is also present in the gas stream with

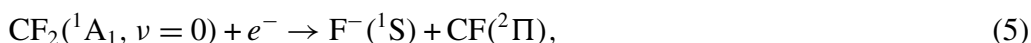
$$\sigma_A^- = \frac{n_B}{n_A} \frac{I_{a-}}{I_{b-}} \sigma_B^- = \frac{I_{B^+} \sigma_A^+ I_{a-}}{I_{A^+} \sigma_B^+ I_{b-}} \sigma_B^-, \quad (4)$$

where the relative number density of the neutral reference molecule to the new molecule, n_B/n_A , is equal to the ratio of their positive ion signals, I_{B^+}/I_{A^+} , multiplied by the ratio of their absolute

ionization cross sections, $\sigma_{B^+}/\sigma_{A^+}$. The term I_{a^-}/I_{b^-} is the relative intensity of negative ions a^- and b^- formed in dissociative electron attachment to A and B, and the known absolute cross section for b^- formation is σ_B^- .

Although a peak originating from dissociative electron attachment to CF_2 was not observed in the negative ion spectrum, a maximum dissociative electron attachment cross section can be estimated if it is assumed that all the F^- signal at 1.8 eV is from CF_2 , where 1.8 eV is chosen as it is close to the threshold for F^- formation from CF_2 . The reference molecule here is CS, which has a known dissociative electron attachment cross section for S^- formation at 5.43 eV, 0.025 \AA^2 [12], and known electron impact ionization cross sections of 0.7, 1.4 and 2.15 \AA^2 at 13, 15 and 17 eV, respectively [32, 33]. Ionization cross sections for CF_2 of 0.03, 0.143 and 0.257 \AA^2 at 13, 15 and 17 eV [23, 34] are also used in the calculation; these CF_2 ionization cross sections were calculated with the BEB model [34] and are available online [23]. The calculated CF_2 ionization cross section values are in excellent agreement with experimental values (see [23, 35]).

Using the procedure just described and the data obtained in the experiments with the $\text{C}_3\text{F}_6/\text{SF}_6$ plasma, the maximum dissociative electron attachment cross section close to the thermodynamic threshold at 1.8 eV for the dissociation,



has been estimated to be significantly smaller than $5 \times 10^{-4} \text{ \AA}^2$. The value of the upper limit, $5 \times 10^{-4} \text{ \AA}^2$ at 1.8 eV, does not change significantly if it is, for example, calculated at 2 eV. The upper limit is expected to be correct to within an order of magnitude in the region of the thermodynamic threshold. The limit of $5 \times 10^{-4} \text{ \AA}^2$ is much smaller than the peak value for the dissociation cross section predicted theoretically by Rozum *et al* [5], which was estimated to be 5% of 25.76 \AA^2 at 0.95 eV. This discrepancy may be explained in part by the fact that the thermodynamic threshold for the formation of F^- from CF_2 is situated approximately 1–2 eV above the predicted resonance maximum. At 1.4–1.5 eV, however, a dissociative electron attachment cross section of $\sim 0.04 \text{ \AA}^2$ was predicted (5% of 0.8 \AA^2), which is considerably higher than the experimental upper limit determined here. The experimental results are more consistent with the lower peak resonance energy predicted by Francis-Staite *et al* [7] to be less than 0.1 eV. If the resonance is located close to 0 eV, the thermodynamic threshold for the formation of F^- is nearly 2 eV higher. It seems probable that CF_2 does not form negative fragments upon electron attachment due to this unfavourable energy gap between the position of the resonance and the threshold for F^- . Very weak negative ion formation due to the high energy tail of this resonance may not have been observable in this experiment as other molecules present in the gas stream also give F^- between 1.8 and 2 eV.

3.5. Dissociative electron attachment to CF_2 produced in fast atom reactions

CF_2 was also produced in the reaction of H atoms with CF_3I with the formation of HI and HF, as described in section 2. This process is ‘cleaner’ than the formation of CF_2 from the $\text{C}_3\text{F}_6 + \text{He}$ plasma reaction as fewer side products are present in the sample. For example, there are no high-mass $(\text{CF}_2)_n$ polymers formed. A positive mass spectrum of the gas sample is shown in figure 9; this mass spectrum is the sum of many spectra taken over the ionization energy range of 14.5–20 eV.

The negative ion electron attachment spectrum from this sample is dominated by the I^- peak from HI close to zero electron energy. Very little signal was observed from other negative

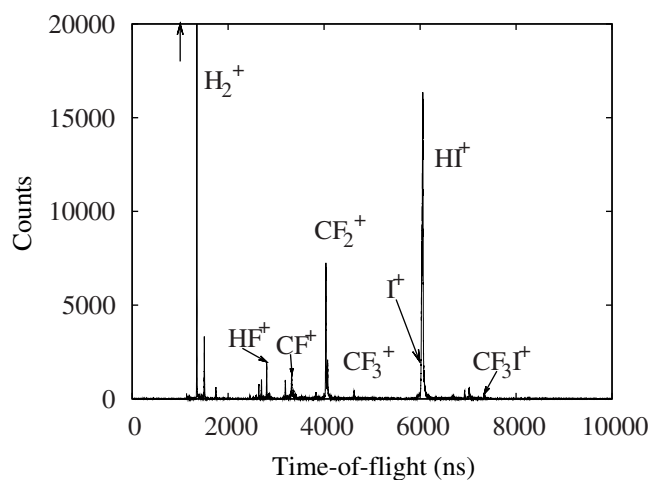


Figure 9. Positive ion signal from the fast atom reaction. Shown is an integrated signal from 14.5 to 20 eV. H_2^+ , CF_2^+ and HI^+ are the strongest signals.

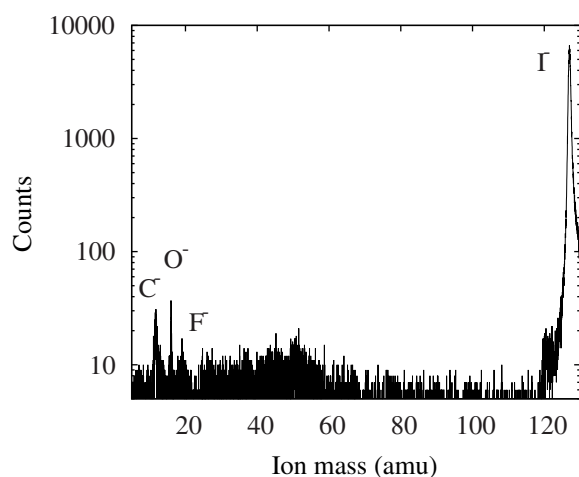


Figure 10. Attachment signal of the CF_2 admixture produced via fast atom reactions. The main signal I^- is from dissociative electron attachment to HI . The O^- and C^- signals are due to residuals in the vacuum chamber.

ions. A composite negative mass spectrum, which is the sum of mass spectra taken over the energy range 0–11 eV, is shown in figure 10; the dominant I^- signal is clearly visible. All the other ions are orders of magnitude weaker by comparison. The O^- peak originates from dissociative electron attachment to residual water vapour in the vacuum chamber and the weak C^- signal may originate from the graphite coating of surfaces inside the apparatus. There is also some noise in the spectrum, principally between 20 and 60 mass units.

A very weak F^- signal is also just visible in figure 10. The variation in intensity of this weak F^- signal with electron energy is shown in figure 11 between 1 and 11 eV; there is very little, if any, signal visible above the noise. It is possible that there is some weak signal due to CF_2 above the predicted threshold of 1.8 eV, but it is weaker than the noise in figure 11.

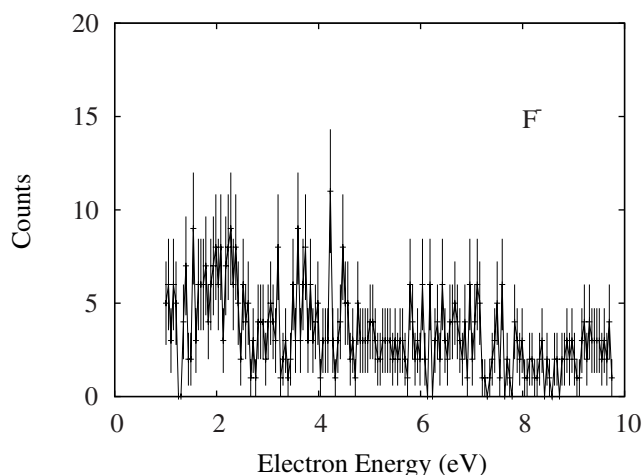


Figure 11. F^- signal observed between 1 and 11 eV from dissociative electron attachment to species produced in the fast atom reaction.

HF is known to form F^- upon electron attachment at 2.5 eV [18]. The dissociative electron attachment cross section of HF, however, is very small, $2 \times 10^{-4} \text{ \AA}^2$ [18]; this cross section is in the same range as the upper value for CF_2 calculated here from the $C_3F_6 + He$ plasma data.

From these fast atom reaction experiments, it seems very likely that either CF_2 forms no negative ions upon electron attachment or the cross section for negative ion formation is very small. An upper limit for the cross section could not be determined from these data due to the lack of a suitable reference molecule in the gas sample.

4. Conclusions

The present experimental investigation has found that F^- formation via electron attachment to the CF_2 molecule has a maximum cross section at least four orders of magnitude smaller than predicted from scattering calculations of Rozum *et al* [5]. This experimental result is consistent with the calculation of Francis-Staite *et al* [7], which predicts a lower electron attachment resonance energy below 0.1 eV, which is lower than the value of 0.95 eV predicted by Rozum *et al*. It can be concluded that the importance of CF_2 for the formation of negative species (F^- , CF^- , F_2^- , C^-) in low-temperature fluorocarbon plasmas is small. As the experiments presented here were carried out under single collision conditions, no information of a possible collisional stabilization of the CF_2^- parent anion was obtained. Without stabilisation, the parent anion is expected to be short lived and was not observed in the experiments carried out here. At much higher gas pressures, it may be possible that the CF_2^- formed by electron attachment may be collisionally stabilized and therefore present in fluorocarbon plasmas.

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References

- [1] Bulcourt N, Booth J P, Hudson E A, Luque J, Mok D K W, Lee E P, Chau F-T and Dyke J M 2004 *J. Chem. Phys.* **120** 9499
- [2] Cunge G and Booth J P 1999 *J. Appl. Phys.* **85** 3952
- [3] Takahashi K, Itoh A, Nakamura T and Tachibana K 2000 *Thin Solid Films* **374** 303
- [4] Stoffels E, Stoffels W W and Kroesen G M W 2001 *Plasma Sources Sci. Technol.* **10** 311
- [5] Rozum I, Limão-Vieira P, Eden S, Tennyson J and Mason N J 2006 *J. Phys. Chem. Data* **35** 267
- [6] Lee M-T, Iga I, Machado L E, Brescansin L M, Castro E A Y and de Souza G L C 2006 *Phys. Rev. A* **74** 052716
- [7] Francis-Staite J R, Maddern T M, Brunger M J, Buckman S J, Winstead C, McKoy V, Bolorizadeh M A and Cho H 2009 *Phys. Rev. A* **79** 052705
- [8] Nikitovic Z D, Stojanovic V D, Booth J P and Petrovic Z 2009 *Plasma Sources Sci. Technol.* **18** 035008
- [9] Maddern T M, Hargreaves L R, Francis-Staite J R, Brunger M J, Buckman S J, Winstead C and McKoy V 2008 *Phys. Rev. Lett.* **100** 063202
- [10] Field T A, Slattery A E, Adams D J and Morrison D D 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** 255
- [11] Linstrom P J and Mallard W G (ed) 2005 *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (available online: <http://webbook.nist.gov> 2006–2008) (Gaithersburg MD: National Institute of Standards and Technology)
- [12] Graupner K, Field T A and Feketeova L 2006 *New J. Phys.* **8** 314
- [13] Heni M and Illenberger E 1986 *Int. J. Mass Spectrom. Ion Process.* **71** 199
- [14] Harland P W and Thynne J C J 1972 *Int. J. Mass Spectrom. Ion Phys.* **9** 253
- [15] Lifshitz C and Grajower R 1972/73 *Int. J. Mass Spectrom. Ion Phys.* **10** 25
- [16] Foner S N and Hudson R L 1978 *J. Chem. Phys.* **68** 2987
- [17] Qian H B and Davies P B 1995 *J. Mol. Spectrosc.* **169** 201
- [18] Gallup G A, Xu Y and Fabrikant I I 1998 *Phys. Rev. A* **57** 2596
- [19] Thrush B A and Zvolenik J J 1963 *Trans. Faraday Soc.* **59** 582
- [20] Rienstra-Kiracofe J C, Tschumper G S, Schaefer H F III, Nandi S and Ellison G B 2002 *Chem. Rev.* **102** 231
- [21] Hiberty P C, Humbel S, Byrman C P and van Lenthe J H 1994 *J. Chem. Phys.* **101** 5969
- [22] Rao M V V S and Srivastava S K 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 1841
- [23] Kim Y-K *et al* 2004 *Electron-Impact Cross sections for Ionization and Excitation* (version 3.0, available online: <http://physics.nist.gov/ionxsec> 2006–2008) (Gaithersburg MD: National Institute of Standards and Technology)
- [24] Christophorou L G 1984 *Electron–Molecule Interactions and their Applications* vol 1 (London: Academic)
- [25] Spyrou S M, Sauers I and Christophorou L G 1983 *J. Chem. Phys.* **78** 7200
- [26] McBride B J, Zehe M J and Gordon S 2002 *NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species* NASA Report <http://gltrs.grc.nasa.gov>
- [27] Li G, Li Q, Xie Y, XU W and Schaefer H F III 2001 *Mol. Phys.* **99** 1053
- [28] Teii K, Hori M, Ito M and Goto T 2000 *J. Vac. Sci. Technol. A* **18** 1
- [29] Stoffels W W, Stoffels E and Tachibana K 1998 *J. Vac. Sci. Technol. A* **16** 87
- [30] Illenberger E and Baumgärtel H 1984 *J. Electron Spectrosc. Relat. Phenom.* **33** 123
- [31] Iga I, Rao M V V S, Srivastava S K and Nogueira J C 1992 *Z. Phys. D* **24** 111
- [32] Freund R S, Wetzel R C and Shul R J 1990 *Phys. Rev. A* **41** 5861
- [33] Sobrinho A M C and Lee M-T 2005 *Int. J. Quantum Chem.* **103** 703
- [34] Kim Y-K, Hwang W, Weinberger N M, Ali M A and Rudd M E 1997 *J. Chem. Phys.* **106** 1026
- [35] Deutsch H, Maerk T D, Tarnovsky V, Becker K, Cornelissen C, Cespiva L and Bonacic-Koutecky V 1994 *Int. J. Mass Spectrom. Ion Process.* **137** 77